Frontier adsorbent science

Drs Laura Espinal and **Dianne Poster** describe the establishment of protocols for ascertaining the fundamental properties of new materials to adsorb carbon dioxide from both single component and complex gases generated by industrial and energy processes

With global emissions of carbon dioxide (CO_2) reaching 34 billion tonnes in 2011, it is critical that an international agreement is made in climate negotiations. How is your research contributing to this complex objective?

Because of the interest in curtailing CO_2 emissions from stationary sources (for example, fossil fuel-fired power generation, steel production and natural gas purification), there is increased emphasis on developing cost-efficient materials that capture CO_2. At the National Institute of Standards and Technology (NIST), we are playing an important role in supporting the discovery and development of adsorbents for CO_2 capture, and other materials related to sustainable industrial processing. Our measurement science and standards efforts will enable reliable measurement of CO_2 sorption data, which will not only enable an even-handed comparison of CO_2 mitigation strategies, but also serve as catalyst for *in silico* CO_2 capture materials innovation. Both are paramount considerations in deliberations on climate change.

Could you explain how a deeper understanding of materials-related measurements, standards and data may provide critical information for CO_2 separation materials?

Optimising next-generation CO_2 capture materials is difficult because many exhibit complex CO_2/sorbent interactions which are not yet fully understood. Our objective is to provide the scientific community with methods and tools that produce accurate and precise sorption measurements, which in turn reveal sorption mechanisms. Using such information, scientists can improve and validate computational tools, resulting in improved materials. The bottom line is that our ability to observe and measure the performance of CO_2 capture materials provides materials developers with 'in place' sorption measurements to keep pace with ever-accelerating product development cycles, ultimately driving technological innovation. If you can properly measure a material's properties, you can control and reliably manufacture it. NIST's unique role is in addressing the challenges inherent to measuring sorption properties of CO_2 capture materials by developing the appropriate standards and characterisation methods, and creating the tools to analyse measurement uncertainties. NIST's role is important not only to capture materials in this sector, but also to those in the trades of fuels, photonics, conversion chemicals and additive manufacturing.

What sparked your interest in the area of adsorbent materials?

While looking for new research areas that harnessed material and chemical sciences for sustainable development, adsorbents were the material of choice for various reasons. First, adsorbents played a key role in technologies that increase environmental quality in the energy sector, including hydrogen and methane storage, CO_2 capture and natural gas purification. In addition, advancing measurement science in the field of adsorption was a great avenue to synergistically combine in-house, world-class expertise from two distinct research areas: engineered materials and gas/solid interactions.

Could you explain the key objectives of NIST's Facility for Adsorbent Characterisation and Testing (FACT)?

While advances are being made to improve current and develop new materials for various industrial sustainable applications such as CO_2 capture, the pace of innovation is significantly stunted by a lack of reproducibility in sorption isotherm measurements, particularly at high pressure, because of a lack of standardised protocols and sample activation methods. FACT supports programmes developing adsorbents and serves the sorbent materials research community by providing impartial testing and characterisation of material sorption properties, and by disseminating reliable sorbent material property data and measurement best practices.

What is the current status of measurements, standards and data?

Based on a comprehensive literature search and extensive interactions with the carbon capture community, we have identified several research gaps related to measurement standards. These gaps currently limit the extent to which solvents, adsorbents (solid sorbents) and membranes can be optimised. We have begun to address these gaps. For example, NIST is working on establishing an experimental parameter-space for evaluating the sorption properties of adsorbents that, when combined with computational methods, would enable a materials-by-design approach. We are also working on the development of a suite of *in situ* characterisation tools to capture a snapshot of the complex interaction between the adsorbent material and the CO_2 molecules.

Are there any significant benefits afforded by basing your research at FACT?

FACT houses instruments for characterising the pore architecture and evaluating fundamental sorption properties of materials upon exposure to single gases, and binary or multicomponent gas mixtures. The instruments use different measuring principles, making it possible to cross-check results. The availability of complementary measurement technologies in a single laboratory and capability to measure preferential adsorption from gas mixtures makes this laboratory a unique venue for exploring the frontiers of adsorption science.

How fundamental is a collaborative approach to your work?

Advancing measurements and standards in adsorption science involves working with a range of materials scientists, computational scientists, adsorbent developers and instrument manufacturers. We are in constant communication with stakeholders from government, industry and academia to discuss strategies by which NIST's expertise and investments can be tailored to support their work. Ultimately, our work aims to accelerate the pace at which our collaborators take their materials discoveries from research to commercialisation, by providing them with methods and tools that yield the reliable data needed to make well-informed decisions. NIST is uniquely poised to provide private-sector manufacturer and adsorbents users with the tools to make accurate and precise measurements.

Material facts

The **Facility for Adsorbent Characterisation and Testing** at the National Institute of Standards and Testing in Maryland, USA, aims to further industrial, energy and environmental sustainability by delivering clear evidence of the gas separation properties of new, commercially viable adsorbent materials

GLOBAL EMISSIONS OF carbon dioxide (CO_2) have risen over the last decade by nearly 3 per cent per year and, in 2011, rose to an unprecedented high of 34 billion tonnes. Without effective intervention, the annual pattern of increasing concentrations is expected to continue. The industrial and power sectors are therefore currently under intense pressure to curb CO_2 and other greenhouse gas emissions in a drive to safeguard the Earth's atmosphere from irreversible change. However, the world population surge to 9 billion people by 2050 will inevitably entail requirements for additional industrial production and power generation, with a concomitant surge in CO_2 emissions and negative impact on the environment.

Potential means of extracting CO_2 from the exhaust streams of stationary sources such as cement production plants and gas wells include solvents, membranes or solid materials with specific adsorbent properties. The basic criteria for the successful adoption of any such technology are cost-effectiveness, efficiency, technological compatibility and kindness to the environment. It is in these terms that membrane and solid sorbent – termed adsorbent – materials hold particular promise. While solvent-based carbon capture systems are currently used extensively, their energy efficiency is low due to their high operating temperatures, as materials scientist Dr Laura Espinal explains: "Conventional solvent-based technologies require significant energy for regeneration, because of the large amount of water (70 per cent by weight) required to maximise the chemical stability of materials in direct contact with the liquid solution". As a consequence, new materials to support carbon management and sequestration technologies that do not involve solvents are expected to play a crucial role in mitigating the effects of increasing CO_2 emissions in the future.

THE FACT FACILITY

Espinal has conducted extensive investigations of the performance of various membrane and solid materials in separating CO_2 from gases, with the aim of enabling speedier development of economic and reliable greenhouse gas capture and storage processes. In 2013, she and colleagues conducted a review of the status of the measurements, standards and data available about solvent, membrane and adsorbent materials that are essential for informing the design of future CO_2 capture techniques. This led Espinal to focus on adsorbents in particular, and she is now head of the new Facility for Adsorbent Characterisation and Testing (FACT) set up by the US National Institute of Standards and Technology (NIST) with support from the US Department of Energy Advanced Research Projects Agency-Energy. The mission of FACT is to address the prevailing lack of quantitative information about the characteristics of adsorbent materials for a range of applications, from photonics to fuel technologies as well as greenhouse gas mitigation: "Our instrumental capabilities and expertise in adsorption sciences put us in a good position to identify and address adsorption measurements that lack reproducibility, a failing that currently limits the pace of materials innovation," observes Espinal.

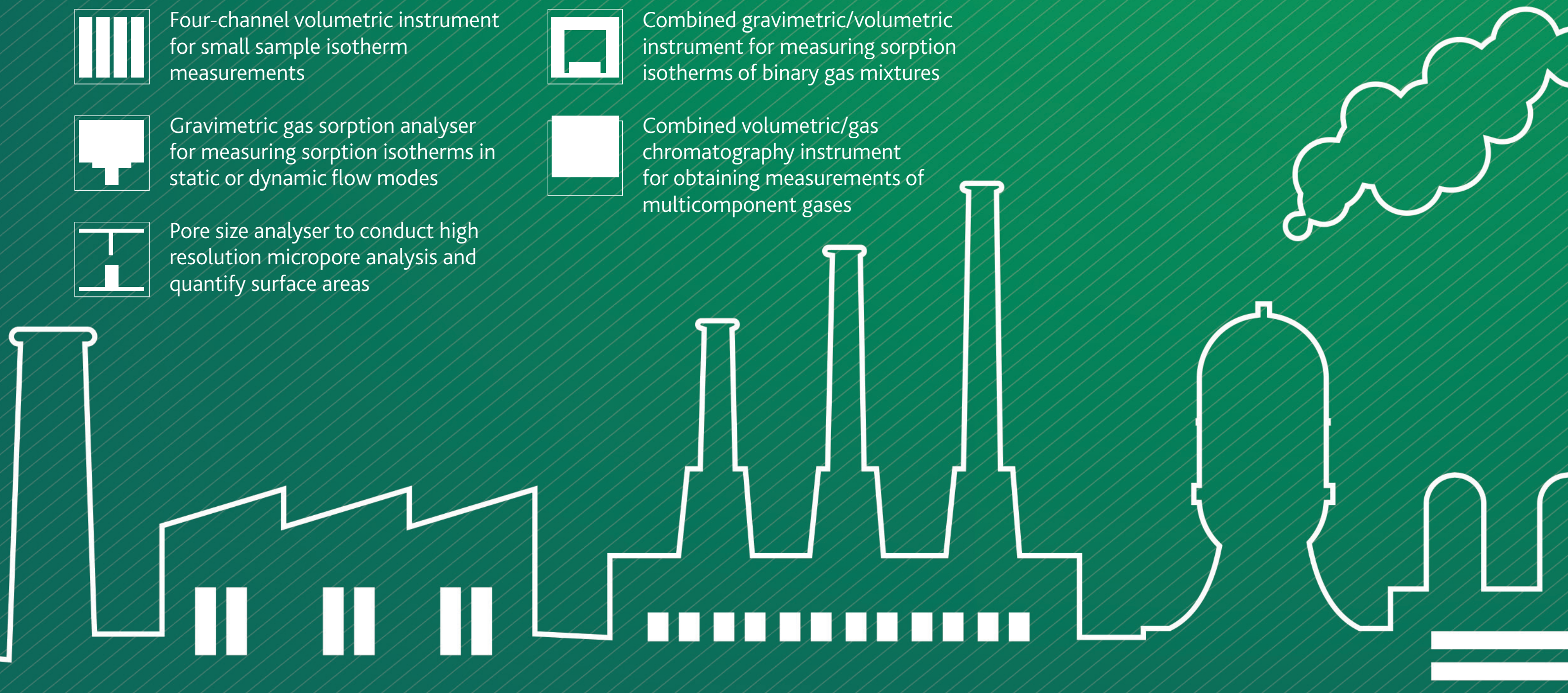
OPTIMISING MATERIAL PROPERTIES

Espinal's review of the state of the art in terms of measurements, standards and data on CO_2 capture materials identified that there was no consensus on how their sorbent attributes should be evaluated. Well-established *in situ* experimental tools for structural characterisation of changes in active solid porous materials, as they happen during CO_2 adsorption, were also lacking. In her role at FACT, and with the help of collaborators, she aims to address these gaps with the appropriate tools, data and protocols.

Since optimisation of a specific material for higher performance rests on valid and verifiable measures of its effectiveness and characteristics under certain conditions, as well as the reproducibility of test results, the FACT team aims to standardise sample activation and testing protocols, especially for sorption isotherm measurements at high pressures.

FACT Instruments

- Four-channel volumetric instrument for small sample isotherm measurements
- Gravimetric gas sorption analyser for measuring sorption isotherms in static or dynamic flow modes
- Pore size analyser to conduct high resolution micropore analysis and quantify surface areas
- Combined gravimetric/volumetric instrument for measuring sorption isotherms of binary gas mixtures
- Combined volumetric/gas chromatography instrument for obtaining measurements of multicomponent gases



Magnetic suspension balance monitors mass uptake without making contact with sample holder.

Using FACT's instruments, it is possible to characterise the pore architecture of a material and evaluate its sorption properties in response to gases with two or more components, as well as single gases. Programmes concerned with developing new adsorbents can collaborate with FACT researchers to determine material sorption properties. For example, FACT recently supported the synthesis of a new porous material in a programme from Professor James Tour's laboratory at Rice University in Texas by providing detailed CO_2 sorption measurements. This new material, composed of carbon with sulphur or nitrogen, can selectively extract and polymerise CO_2 under the pressures present in natural gas flowing at well heads with no effect on the quality of the natural gas produced. Importantly, as the material can be regenerated at ambient temperatures, the process operates with much lower energy requirements than current high-temperature extraction methods and has received attention as a viable proposition for making natural gas extraction more cost-effective and environmentally friendly.

INSTRUMENTATION AT FACT

The five main instruments housed in FACT use different measurement principles, while their measurement capabilities are complementary. In addition, they can operate at a wide range of temperatures and pressures; and Espinal's team is currently developing *in situ* material characterisation techniques that will enable them to capture snapshots of the behaviours of adsorbents upon interactions with various gases under experimental conditions at selected pressures and temperatures.

According to Espinal, it is the ability of FACT to obtain complementary measures from these multiple instruments in a single laboratory and the capacity to measure adsorption propensities in gas mixtures that overcomes the usual difficulty in adsorption science to determine the sorption of a material upon exposure to a gas mixture: "We have capabilities to simultaneously measure mass change and pressure drop within a single instrument," she states. "This enables, for example, the measurement of sorption properties of a material in the presence of a binary mixture by solving a matrix with two unknowns and two equations."

LOOKING AHEAD

As their testing of single, binary and multicomponent gases against a variety of materials proceeds, the FACT team will be generating reliable gas sorption isotherm data pertaining to the properties of each sorbent material. They are keen to share these outputs with the adsorption science community through peer-reviewed publications and also to disseminate the best practices that they are developing in testing and measurement methods and procedures.

The FACT team recently hosted, with the US Council for Chemical Research, a workshop to identify measurement research needs in the areas of adsorbent characterisation, gas storage and gas separations. Information from this workshop will provide input to a future workshop-dialogue with the carbon capture materials community. Both of these activities will provide information about the research and standards activities of FACT, the facility's independent testing and measurement services, and efforts to advance *in situ* characterisation of CO_2 adsorbent materials.

INTELLIGENCE

MEASUREMENTS, STANDARDS AND DATA NEEDS FOR CO_2 CAPTURE MATERIALS

OBJECTIVES

To support programmes developing adsorbents for various industrial sustainable applications, such as CO_2 capture, by providing impartial testing, establishing testing procedures, disseminating sorbent material property data and measurement best practices, and developing tools for the *in situ* characterisation of multi-scale porous materials upon exposure to various gases at industrially relevant temperatures and pressures.

KEY COLLABORATORS

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LAURA ESPINAL is a materials scientist at NIST. Her scientific interests include advancing sorption measurement science and *in situ* structural techniques to enable the rational design of advanced materials for sustainable energy and environmental applications, including CO_2 capture, through an integrated experimental and computational approach.

DIANNE POSTER is special assistant to the acting director of NIST, supporting emerging issues for measurements, standards, technology and data in the chemical, materials and environmental sciences. In a prior assignment, as Deputy Associate Director for Technology and Environmental Policy at the White House Council on Environmental Quality, Poster administered the environmental federal regulatory portfolio and advised on policy and strategy issues related to protecting the environment.